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硕 士 学 位 论 文

原位研究吸附于红树叶片表面上多环芳烃
的光降解及环境行为

In situ study on the photodegradation of PAHs adsorbed on
the surfaces of mangrove leaves and their environmental
behaviors

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摘要

红树林 (Mangrove) 是热带、亚热带海岸重要的湿地生态系统, 因生产力高、富含有机质以及强还原性环境条件等特性, 使之成为吸收和积累多环芳烃 (Polycyclic Aromatic Hydrocarbons, PAHs) 的理想场所。植物对周围环境有着高度的依赖性, 尤其是植物叶片能通过干、湿沉降及气体扩散等作用有效富集和累积空气中的PAHs, 且表面积大、蜡质含量高的叶片表现出较高的富集效率。红树植物为适应其特殊的生境, 大部分叶片都具有表面积大和角质层厚等特点, 因此, 深入研究吸附在红树叶片表面上PAHs的环境行为及其在红树体内的迁移过程等具有重要的环境意义。本论文的主要研究内容和结果包括以下几个方面:

(1) 新建的光纤荧光法定量测定了吸附于白骨壤 (*Avicennia marina*, *Am*)、海漆 (*Excoecaria agallocha*, *Ea*)、秋茄 (*Kandelia candel*, *Kc*)、桐花树 (*Aegiceras corniculatum*, *Ac*) 和老鼠勒 (*Acanthus ilicifolius*, *Ai*) 叶片表面上的荧蒽 (fluoranthene, *Fla*)。结果表明: 测定吸附于 *Am*、*Ea*、*Kc*、*Ac* 和 *Ai* 叶片表面上 *Fla* 的线性范围分别为 2.5-500、2.0-600、4.5-1100、15-600 和 3.5-450 ng/spot, 检出限分别为 0.91、0.63、1.12、3.52 和 1.40 ng/spot, 相对标准偏差 (RSD) 均小于 7.79 % (n=15), 回收率依次分别为 97.4-108.5、78.8-96.8、77.0-90.4、84.2-108.0 和 78.4-102.3 %。实验结果表明所建方法具有简单快速、环境友好、省时省力等优点。

(2) 利用 Fluovision 荧光测定系统 (带光纤附件) 法定量测定了吸附于 *Am*、*Ea* 和 *Kc* 叶片表面上的 *Fla*。结果表明: 测定吸附于 *Am*、*Ea* 和 *Kc* 叶片表面上 *Fla* 的线性范围分别为 0.8-350、1.0-300 和 0.25-150 ng/spot, 检出限分别为 0.0438、0.167 和 0.0107 ng/spot, RSD 均小于 6.4 % (n=9), 回收率分别为 99.4-111.8、96.7-100.1 和 91.8-114.8 %。以上实验结果表明该方法具有较高的灵敏度和很好的精密度。

(3) 利用所建立的光纤荧光法研究了吸附于三种红树叶片正面上不同量 *Fla* 的光降解行为。结果表明: 吸附于不同红树叶片上 *Fla* 的光降解均遵循一级反应动力学模式, *Fla* 的光解速率大小为 $Ac > Ea > Kc$; 不同红树叶片的蜡质对汞灯发射光的吸收程度不同, 这也是导致不同红树叶片上 *Fla* 光解速率不同的一个重要因素; *Fla* 的起始浓度不影响其光解速率。实验结果表明, 吸附于红树叶片上的

Fla可以发生光降解,而且是吸附于红树叶片上Fla的一个重要环境行为,Fla因挥发和叶片吸收而减少的量相对较少,二者的和仅占光降解的Ea 6.23 %、Kc 8.65 %、Ac 6.26 %。

(4) 用光纤荧光法首次实现了原位同时定量测定吸附于活体Kc幼苗叶片表面上的Flu、Phe和Fla。实验结果表明:测定吸附于Kc幼苗叶片表面上三组分Flu、Phe和Fla的线性范围分别为:35-700、5-900和2-450 ng/spot,检出限分别为9.11、1.65和0.90 ng/spot, RSD分别为10.32、7.56 和 4.29 %,回收率分别为83.0-91.2, 78.5-88.5和91.5-107.3 %。实验结果表明该方法具有简单、省时、准确、灵敏度高、环保等优点。

(5) 用(4)中所建的方法,在实验室条件下首次研究了吸附于Kc幼苗叶片表面上三组分PAHs在单独和混合条件下的光降解行为,同时考察了PAHs因挥发和叶片吸收而减少的量。实验结果表明:吸附于Kc幼苗叶片表面上三组分PAHs在单独和混合条件下的光降解均遵循一级反应动力学模式,其光降解速率大小为Flu>Fla>Phe;在混合条件下三组分PAHs的光降解存在拮抗作用,其光降解速率分别比单组分慢Flu 13.8 %、Phe 19.0 %、Fla 15.5 %;实验结果还表明光降解是吸附于Kc幼苗叶片表面上三组分PAHs消失的主要途径,三组分PAHs因挥发和叶片吸收而减少的量相对较少,二者的和仅占光降解的Flu 7.75 %、Phe 11.8 %、Fla 14.2 %。

(6) 用所建立的光纤荧光法,在实验室模拟生态条件下,原位研究了生态箱中Phe和Fla在Am幼苗叶片的含量变化过程,同时用荧光显微技术研究了Phe和Fla在Am幼苗体内的迁移过程及最终贮存位置。实验结果表明,由于受到温度、光照、风速、相对湿度等因素的影响,在一个月实验周期内,Phe和Fla在Am幼苗叶片表面不存在明显的吸附平衡状态;吸附在Am幼苗叶片表面的Phe和Fla会进一步往Am幼苗体内迁移,由于两者理化特性及对Am幼苗的植物毒性不同,其在Am幼苗体内的迁移速率不同,其中Phe的迁移速率大于Fla;二者在Am幼苗体内的迁移路径大致相同;吸附在Am幼苗茎表面和远轴面的Phe和Fla均不易往内部组织迁移,吸附在近轴面的Phe和Fla较易往叶片内部迁移;生态箱空气中同时有气态和颗粒态的Phe和Fla吸附在叶片表面上。

本研究结果将为红树林湿地的环境风险评价提供重要的科学依据,也为更好

地保护和利用红树林资源提供一定的科技支撑,同时为红树林生态系统的环境规划和环境管理提供可靠的依据,具有重要的科学意义和环境效益。

关键词: 光降解; PAHs; 光纤; 荧光法; 红树叶片

厦门大学博士论文摘要库

Abstract

The mangrove ecosystem is an important intertidal estuarine wetland along tropical and subtropical coastlines. The unique features of mangroves such as high primary productivity, rich organic carbon and anoxic conditions make them an ideal 'sink' for uptake and preservation of PAHs. Plants have a high degree of dependence on the surroundings. In particular, plant leaves can enrich and accumulate atmospheric PAHs through dry or wet deposition and gas diffusion. And leaves with large surface area and high lipid containing have higher accumulating efficiency. Mangrove, in order to meet their specific habitats, most of their leaves have large surfaces and thick cuticles, therefore, it is of great environmental value to study the environmental behaviors and the migration processes of PAHs adsorbed on mangrove leaves. Research contents and results in this paper are as follows:

(1) A fiber optical fluorimetry for determination of fluoranthene(Fla) adsorbed onto the surface of five kinds of mangrove leaves was established. Experimental results showed that the linear dynamic ranges for determination of Fla adsorbed onto *Avicennia marina*(Am), *Excoecaria agallocha*(Ea), *Kandelia candel*(Kc), *Aegiceras corniculatum*(Ac) and *Acanthus ilicifolius*(Ai) leaves were 2.5-500, 2.0-600, 4.5-1100, 15-600 and 3.5-450 ng/spot, with detection limits of 0.91, 0.63, 1.12, 3.52 and 1.40 ng/spot, respectively, and with relative standard deviations less than 7.79 % (n=15). The experimental recovery results for Fla adsorbed onto Am, Ea, Kc, Ac and Ai leaves were 97.4-108.5, 78.8-96.8, 77.0-90.4, 84.2-108.0 and 78.4-102.3 %, respectively. Experimental results showed that the established method had the merits of simple, rapid, environmentally friendly, time and labor saving.

(2) Fla adsorbed on the surfaces of Am, Ea and Kc leaves were quantitatively determined by Fluovision fluorescence measured system coupled with optical fiber. Experimental results showed that the linear dynamic ranges for determination of Fla adsorbed onto Am, Ea and Kc leaves were 0.8-350, 1.0-300 and 0.25-150 ng/spot, with detection limits of 0.0438, 0.167 and 0.0107 ng/spot, respectively, and with relative standard deviations less than 6.4 % (n=9). The experimental recovery results for Fla adsorbed onto Am, Ea and Kc leaves were 99.4-111.8, 96.7-100.1 and 91.8-114.8 %, respectively. Experimental results showed that the newly established

method was of high sensitivity and precision.

(3) With the established fiber-optic fluorimetry, the photodegradation processes of different initial concentrations of Fla adsorbed on the upper leaf surfaces of three mangrove species were studied. Results showed that the photolysis of Fla adsorbed on the upper surfaces of mangrove leaves followed first-order kinetics with photolysis rates in the order of $Ac > Ea > Kc$. The different absorption characteristics of leaf-wax played an important role in the different photolysis rates of Fla adsorbed on these three mangrove species. The different initial concentrations of Fla adsorbed on the selected mangrove leaves did not affect the photolysis rates of Fla. Experimental results showed that Fla adsorbed on mangrove leaves can be photolyzed, and photolysis was found to be the main transformation pathway for the Fla adsorbed on mangrove leaves, whereas disappearance of the adsorbed Fla as a result of volatilization and absorption could be negligible, which were only 6.23 %, 8.65 %, 6.26 % for Ea , Kc and Ac compared to the amount of photolysis;

(4) A fiber-optic fluorimetry for *in situ* simultaneous determination of fluorine (Flu), phenanthrene (Phe) and fluoranthene (Fla) adsorbed on the leaf surfaces of Kc seedlings was developed. Experimental results showed that the linear ranges for determination of Flu, Phe and Fla adsorbed on Kc leaves were 35-700, 5-900 and 2-450 ng/spot, respectively. The detection limits for Flu, Phe and Fla were 9.11, 1.65 and 0.90 ng/spot and with the relative standard deviations 10.32 %, 7.56 % and 4.29 % ($n = 9$), respectively. The recovery results for Flu, Phe and Fla adsorbed on Kc leaves were 83.0-91.2, 78.5-88.5 and 91.5-107.3 %, respectively. These results showed that the established method is simple, time-saving, sensitive and environmentally friendly, etc.

(5) Under the laboratory experimental conditions, the photolysis processes of Flu, Phe and Fla individual and in mixtures adsorbed on the leaf surfaces of living Kc seedlings were studied. Meanwhile, the disappearance of Fla resulted from evaporation and leaf absorption was also studied. Results showed that the photolysis of Flu, Phe and Fla individual and in mixtures adsorbed on the leaf surfaces of Kc

seedlings followed first-order kinetics with photolysis rates on the *Kc* leaves in the order of Flu>Fla>Phe. An antagonistic effect was found when the three PAHs were coexisted adsorbed on living *Kc* seedlings with Flu, Phe and Fla photolysis rates 13.8 %, 19.0 % and 15.5 % lower than the three of them together. The experimental results also indicated that photolysis was the main transformation pathway for Flu, Phe and Fla both individual and in mixtures adsorbed on *Kc* leaves, whereas disappearance of the adsorbed Flu, Phe and Fla as a result of volatilization and leaf absorption could be negligible which were only 7.75 %, 11.8 % and 14.2 % for Flu, Phe and Fla compared to the amount of photolysis during the experimental period.

(6) Simulating the natural ecosystem conditions, the amount changing processes of Phe and Fla on the leaf surfaces of *Am* seedlings in the eco-boxes were studied in the lab by the fiber-optic fluorimetry. Meanwhile, the distribution changing processes and the final location of them were studied by fluorescence microscope. Experimental results showed that because of the effects of temperature, illumination, wind speed, relative humidity and plant growth dilution, during the one month experimental period, there was no obvious adsorption equilibrium for the Phe and Fla adsorbed on the leaf surfaces of *Am* seedlings. Phe and Fla adsorbed on the leaf surfaces of *Am* seedlings can migrate into the inner parts of *Am* seedlings, but the migration rates were different with Phe faster than Fla because of the different physicochemical properties and biology toxicities. The migration pathways of Phe and Fla in the *Am* seedlings were almost the same. Phe and Fla adsorbed on the surface of stem and abaxial side were hard to migrate into the inner parts of *Am* seedlings compared to those of adsorbed on the adaxial sides of *Am* leaves. Both gaseous and particulate Phe and Fla were observed on the leaf surfaces of *Am* seedlings.

The researches provide an important scientific basis for the environmental risk assessment of mangrove wetland and a scientific and technological support for the protection of mangrove resources. Meanwhile, the researches provide reliable information for estimating, programming and management of mangrove ecosystem and have essential scientific and environmental benefits.

Keywords: photodegradation; PAHs; fiber-optic; fluorimetry; mangrove leaves

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